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Studies on the Hydrolysis of Metal Ions

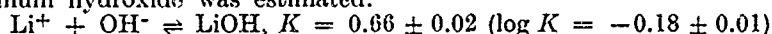
Part 49. An emf Study of Lithium Hydroxide in 3 M (NaClO₄) Medium

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An emf study has been made in a system of various concentrations of lithium and hydroxide ions in sodium perchlorate medium using a hydrogen electrode at 25°C. The general composition of the cell is $\text{Pt}|\text{H}_2, B \text{ M Li}^+, (3-B) \text{ M Na}^+, A \text{ M OH}^-, (3-A) \text{ M ClO}_4^-|\text{Ref}$ where

$\text{Ref} = | 3 \text{ M NaClO}_4, 2.99 \text{ M Na}^+, 0.01 \text{ M Ag}^+, 3 \text{ M ClO}_4^-|\text{AgCl}, \text{Ag}$
From the difference in emfs between sodium hydroxide solutions with and without lithium ions, the following formation constant of lithium hydroxide was estimated:



Lithium hydroxide has usually been considered to be a strong base, almost completely dissociated in aqueous solution, like sodium hydroxide or potassium hydroxide.

In 1879, Kohlrausch¹ suggested an association of lithium ions with hydroxide ions from his conductivity measurements. Calvert² also suggested the existence of a lithium hydroxide complex and Harned and Swindells³ assumed the presence of it in aqueous solution in order to explain their activity data.

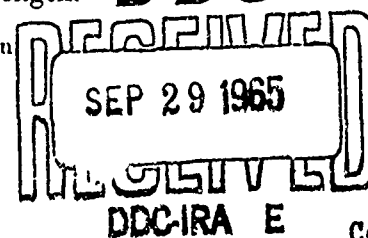
The work by Kolthoff⁴ in 1923 was the first systematic survey to determine the formation constant

$$K = [\text{LiOH}]/[\text{Li}^+][\text{OH}^-] \quad (1)$$

of lithium hydroxide. The average value obtained in media of various concentrations of lithium chloride and sulfate was $K = 2$ (18°C, corrected to zero ionic strength).

Darken and Meier,⁵ who investigated conductivities of aqueous alkali halide solutions, concluded in 1942 that lithium hydroxide is associated, in contrast to sodium and potassium hydroxide, and that the formation constant is $K = 0.83$ extrapolated to zero ionic strength.

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Gimblett and Monk⁶ calculated formation constants of some alkali and alkaline earth hydroxides using the emf data of Harned and coworkers.^{7,8} At 25°C the formation constant of lithium hydroxide corrected to zero ionic strength was found to be 1.5₃ (in lithium chloride medium⁷) and 1.4₃ (in lithium bromide medium⁸).

Kakihana, Mori and Nomura⁹ observed that the ion exchanger affinities of isotopes of lithium ions in lithium hydroxide solution were slightly different from those of the lithium isotopes in lithium chloride solution. By accurate mass-spectrometric measurements they undertook to find the difference between the formation constants of ⁶LiOH and ⁷LiOH.

In the study of a very weakly associated hydroxide complex, experiments must be made with solutions of rather high pH and of relatively high metal concentration. Therefore, difficulties may arise from the dissolution of glassware into the test solution, absorption of carbon dioxide, and impurities in both the medium salt and the metal ion solutions. Moreover, the numerical values of the formation constants obtained for such very weakly associated complexes are affected significantly by the assumptions made in deriving them, as has already been pointed out by Bates and his coworkers¹⁰ and by Carell and Olin.¹¹

In the last fourteen years precise methods for studying the hydrolysis of metal ions have been developed in this laboratory. Among other things very careful methods for preparing medium salts and metal solutions have been developed. With the help of this general background the present investigation was carried out to add a little more information on the behavior of lithium hydroxide in aqueous solution. This work has followed a plan similar to that of Carell and Olin.¹¹

Symbols

A	total concentration of OH^-
a	concentration of free OH^-
B	total concentration of Li^+
b	concentration of free Li^+
K	formation constant of lithium hydroxide in the reaction $\text{Li}^+ + \text{OH}^- \rightleftharpoons \text{LiOH}$
E	emf; E_{0a} and E_{0r} , constants; E_j , liquid junction potential
f	activity factor
k_a, k_b	constants
X	concentration of halide ions

REAGENTS AND ANALYSES

Lithium perchlorate solution was prepared according to Biedermann and Ciavatta;¹² thus the saturated solution of lithium perchlorate prepared by addition of HClO_4 to Li_2CO_3 was made slightly alkaline (pH~8) by adding a small amount of LiOH , left to stand over night and then filtered. The pH of the solution was decreased to about 3 by addition of dilute HClO_4 , and the solution was boiled to expel CO_2 and to concentrate. Crystals of LiClO_4 were formed on cooling the solution. They were recrystallized twice from water.

The concentration of a lithium perchlorate solution was determined in three ways: (1) passing a weighed amount of the lithium perchlorate solution through a cation exchange resin, Dowex 50 in the hydrogen form and titrating the eluate with standardized NaOH; (2) direct drying of the lithium perchlorate solution under an infrared lamp and then in an air bath at 105°C and weighing; (3) adding H_2SO_4 to the lithium perchlorate solution, fuming off HClO_4 and weighing as the sulfate. These results agreed within $\pm 0.03\%$ (percent average deviation).

The small excess of acid in the lithium perchlorate was determined by titration with standardized sodium hydroxide using a Gran plot¹³; it was taken into consideration when the analytical concentration of hydroxide ions in the solution was calculated. Sodium perchlorate solution was prepared from sodium carbonate by the method described by Biedermann.¹⁴ Thus, a slight excess of concentrated perchloric acid was added to sodium carbonate, which had been recrystallized twice from water. The solution was boiled to remove CO_2 , neutralized with NaOH to pH ~ 8, allowed to stand for a few days and any residue was filtered off. The solution was acidified again with HClO_4 and boiled. The pH of the solution was adjusted to be approximately neutral. The sodium perchlorate was recrystallized once from the solution.

The concentration of a sodium perchlorate solution was determined both by direct drying under an infrared lamp and then in an air-bath, and by using the ion exchange resin, Dowex 50.

The excess concentration of acid in a sodium perchlorate solution was determined in the same way as for a lithium perchlorate solution.

Perchloric acid solution was prepared from HClO_4 (p.a.) and standardized against potassium hydrogen carbonate, which had been recrystallized twice from KHCO_3 (Merck p.a.) and dried in an atmosphere of CO_2 .

Sodium hydroxide solution of 50 % was prepared from p.a. material, filtered through a G4 Jena glass filter, and stored in a polyethylene bottle filled with N_2 . Dilute solutions were prepared from de-aerated water and the 50 % stock solution. The solutions were standardized against HClO_4 , which had been standardized in turn against KHCO_3 , using a Gran plot in each experiment.

Silver perchlorate solution was prepared by adding an excess of Ag_2O to a boiling HClO_4 solution. The solution was filtered, and the concentration of Ag^+ was determined by precipitating AgCl and weighing it.

APPARATUS

The titration cell used was of the "Wilhelm" type described by Forsling, Hietanen and Sillén.¹⁵

Hydrogen electrodes were made according to Bates.¹⁶ The hydrogen gas used for hydrogen electrodes was passed through "desoxo" and activated copper and then through 10 % H_2SO_4 , 10 % NaOH, and 3 M NaClO_4 solutions.

Silver chloride and bromide electrodes were prepared by Brown's method.¹⁷

The potentiometer used was a Vernier Potentiometer, Cambridge Instrument Co. Ltd., England. Hundredths of a mV were estimated in each case.

A Jena glass titrating vessel was used without paraffinizing.

EXPERIMENTAL PROCEDURE

All emf measurements were carried out at $25.00 \pm 0.05^\circ\text{C}$ in a paraffin-oil thermostat, which was placed in a thermostated room at approximately 25°C . The emf measurements with a hydrogen electrode were performed as follows in a typical case, for the "main" series of experiments: The titration vessel was filled with nitrogen gas before the starting solution was introduced. The starting solution consisted of A_0 M NaOH and $(3-A_0)$ M NaClO_4 . The magnitude of A_0 was varied from 0.016 M to 0.082 M. The solution was introduced into the vessel from a 50 ml pipet, which had been calibrated and protected against carbon dioxide. During the titration nitrogen gas was replaced with hydrogen gas which was free from oxygen and carbon dioxide and was presaturated with water vapor.

From a buret, 3 M (Li,Na)ClO₄ solution was added to the titration vessel so that [Li⁺] gradually increased whereas [OH⁻] decreased by dilution.

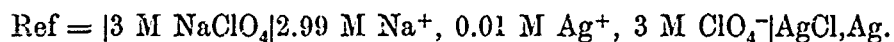
In emf measurements using silver-silver halide indicator electrodes 3 M Na(ClO₄,Cl) was placed in the titration vessel and from the buret were added 3 M Na(ClO₄,Cl) solutions with different [Cl⁻] or in some cases 3 M (Na,Li)ClO₄ solutions. In these experiments nitrogen gas was employed when the titration vessel was filled.

Each experiment was repeated at least twice.

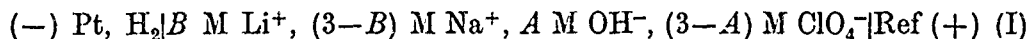
METHOD OF INVESTIGATION

The present investigation was carried out as a series of potentiometric titrations at 25°C in NaClO₄ medium of a total ionic concentration of 3 M.

Hydrogen electrodes, or in some cases silver-silver halide electrodes, were used in combination with the reference half-cell:



In the final experiments to be described below, the cell had the general composition:



The emf for cell (I) can be expressed by the following equation:

$$E = E_{0a} + 59.15 \log a + 59.15 \log f_{\text{OH}} + E_j \quad (2)$$

where

$$a = [\text{OH}^-] \quad (3)$$

In the following, the E data will be treated on the assumption that a is affected by the formation of the complex LiOH. In emf studies, there is no theoretical basis for a strict separation of the effects of variations of activity factors, liquid junction potentials and complex formation. When strong complexes are formed, it seems reasonable to ascribe the larger part of the variation of E to the effect of complex formation. With weak complexes, however, the effect on E of complex formation may be of the same order of magnitude as that of activity factors and liquid junction potentials. So, it is important to state what other assumptions have been made.

ASSUMPTIONS

The following assumptions were made in analyzing the data.

1) Each of the f_{OH} (activity factor) and E_j (liquid junction potential) terms in eqn. (2) can be split into two terms, one of which is a function of $a = [\text{OH}^-]$ and the other a function of $b = [\text{Li}^+]$. With this assumption, eqn. (2) takes the form

$$E = E_{0a} + 59.15 \log a + 59.15 \log (f_{\text{OH}})_a + E_{ja} + 59.15 \log (f_{\text{OH}})_b + E_{jb} \quad (4)$$

2) Na⁺ ions do not form complexes with OH⁻.

3) Na⁺ and Li⁺ do not form complexes with halogenide ions, Cl⁻ and Br⁻.

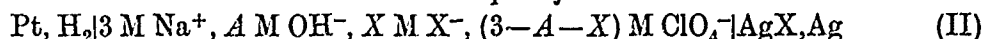
4) The activity factor of free OH⁻ ions, f_{OH} , is equal to that of Cl⁻ or Br⁻ ions in the same medium. This assumption will be discussed below.

5) LiOH is the only complex formed. The formation constant, K , is then defined as

$$K = \frac{[\text{LiOH}]}{[\text{Li}^+][\text{OH}^-]} = \frac{(A-a)}{ab} \quad (1)$$

Test of assumption 4

Carell and Olin¹¹ used a cell without liquid junction:



where $\text{X}^- = \text{Cl}^-$ or Br^- . The emf of cell (II) is

$$E = E_{\text{ox}} - E_{\text{oa}} + 59.15 \log (A/X) + 59.15 \log (f_{\text{OH}}/f_{\text{X}}). \quad (5)$$

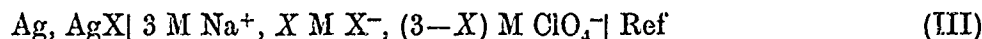
They found that $E - 59.15 \log (A/X)$ was a constant, which may be explained in the simplest way if it is assumed that in these solutions

$$f_{\text{OH}} = f_{\text{X}} \quad (6)$$

This is identical to assumption 4.

The concentration range of OH^- ions, which has been tested by them for assumption 4, was from 0 to 0.03 M.

In the present investigation, this assumption was extended to $A = 0.082 \text{ M}$, for treating the data and it did not seem to introduce serious errors. Some additional measurements were made with the cell



for which

$$E = E_{\text{ox}} + 59.15 \log X + 59.15 \log f_{\text{X}} + E_{\text{jX}} \quad (7)$$

As seen from Fig. 1, the value of $(E - 59.15 \log X)$ is practically constant. The simplest explanation of this result is that, within the limit of experimental error,

$$f_{\text{X}} = 1, E_{\text{jX}} = 0 \quad (8)$$

at least up to $X = 0.2 \text{ M}$.

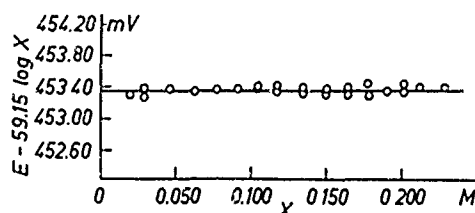


Fig. 1. Plot of $E - 59.15 \log X$ against X in 3 M (Na^+ , $\text{ClO}_4^- + \text{Cl}^-$), cell (III), eqn. (7).

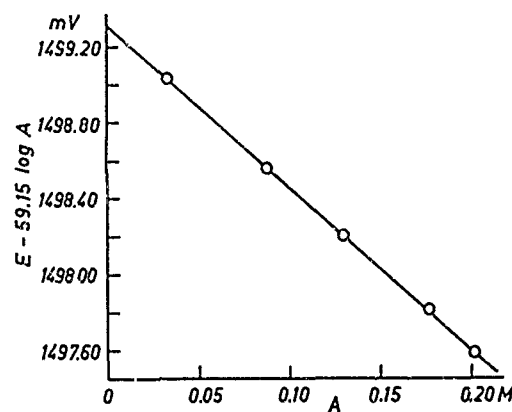
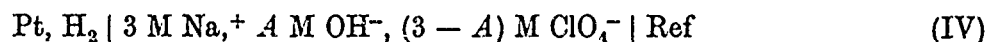


Fig. 2. Plot of $E - 59.15 \log A$ against A in 3 M (Na^+ , $\text{ClO}_4^- + \text{OH}^-$), cell (IV), eqns. (9-10). The slope of the solid line is -8.2 mV/M .

Influence of a on f_{OH} and E_j

A series of experiments were carried out with a cell similar to (I) but without Li^+ , thus $B = 0$, and



for which according to eqn. (2)

$$E = E_{\text{ox}} + 59.15 \log a + 59.15 \log (f_{\text{OH}})_a + E_j \quad (9)$$

Since we have assumed no complex formation in this case, we can set $a = A$, the total concentration of OH^- . A plot of $(E - 59.15 \log a)$ versus a (Fig. 2.) gave a straight line of slope

$$k_a = \frac{d(E - 59.15 \log a)}{da} = -8.2_0 \pm 0.05 \text{ mV/M} \quad (10)$$

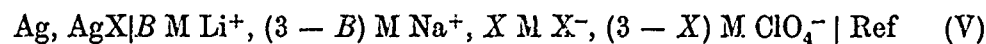
for $a \leq 0.2 \text{ M}$. From this we will conclude that in the range of our experiments

$$59.15 \log (f_{\text{OH}})_a + E_{j,a} = ak_a \quad (11)$$

The value for k_a agrees with those reported in earlier papers.^{11,18,19} The major part of it can be reasonably ascribed to the liquid junction potential.

Influence of the lithium concentration, b ,
on f_{OH} and E_j

Another series of measurements were made with a cell



Again, we split the $\log f$ and E_j terms into two as earlier:

$$E = E_{\text{ox}} + 59.15 \log X + 59.15 \log (f_x)_x + E_{j,x} + 59.15 \log (f_x)_b + E_{j,b} \quad (12)$$

Since we have found earlier, with cell (III), that $59.15 \log (f_x)_x + E_{j,x}$ is negligible, we may rewrite and rearrange (12) as follows:

$$E - 59.15 \log X = E_{\text{ox}} + 59.15 \log (f_x)_b + E_{j,b} \quad (13)$$

Plotting $(E - 59.15 \log X)$ versus $b = B$ (according to our assumptions, Li^+ forms no complexes with halide ions), we find a straight line for $B \leq 0.9 \text{ M}$ with the slope (Fig. 3)

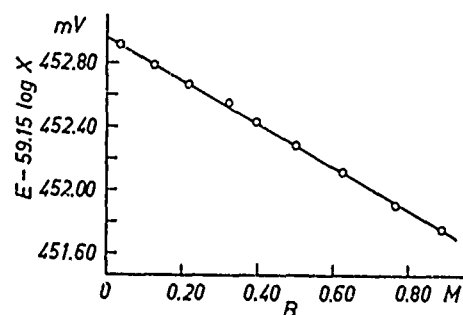


Fig. 3. Plot of $E - 59.15 \log X$ against B in $3 \text{ M (Na}^+ + \text{Li}^+, \text{ClO}_4^- + \text{Cl}^-)$, cell (V), eqns. (13–14). The slope of the solid line is -1.3 mV/M .

$$k_b = \frac{d(E - 59.15 \log X)}{db} = -1.3 \pm 0.3 \text{ mV/M} \quad (14)$$

Thus, for cell (III) we have

$$59.15 \log (f_x)_b + E_{jb} = b \cdot k_b \quad (15)$$

Using our assumption 4) we may conclude that for the solutions in the final experiment

$$59.15 \log (f_{OH})_b + E_{jb} = b \cdot k_b \quad (16)$$

Thus, we will use for the emf of cell (I) the expression (see eqn. (4))

$$E = E_{0a} + 59.15 \log a + a \cdot k_a + b \cdot k_b \quad (17)$$

with $k_a = -8.2 \text{ mV/M}$ and $k_b = -1.3 \text{ mV/M}$.

Determination of K

The data for the final experiments are given in Table 1. The primary data are the total concentrations of Li^+ and OH^- , A and B , respectively,

Table 1. Summary of the experimental results.*

Series Ia. $A \times 10^3 \text{ M}, B \times 10^3 \text{ M}, E \text{ mV}, Z$; 16.66, 0.00, 1393.96, —; 16.33, 3.91, 1393.41, —; 16.01, 7.68, 1392.78, —; 15.42, 14.79, 1391.82, —; 14.86, 21.42, 1390.72, —; 14.34, 27.56, 1389.75, —; 13.86, 33.33, 1388.78, —; 13.10, 38.72, 1387.74, 0.0085; 12.98, 43.77, 1386.87, 0.0078; 12.58, 48.50, 1386.00, 0.0076; 12.20, 52.96, 1385.09, 0.0076; 11.85, 57.18, 1384.24, 0.0079; 11.67, 70.42, 1383.65, 0.0072; 11.34, 95.96, 1382.46, 0.0072; 10.88, 131.67, 1380.86, 0.0064; 10.31, 174.98, 1378.60, 0.0063; 9.68, 223.59, 1376.25, 0.0056; 9.11, 266.70, 1373.96, 0.0052.

Series Ib. $A \times 10^3 \text{ M}, B \times 10^3 \text{ M}, E \text{ mV}, Z$; 16.66, 0.00, 1393.57, —; 16.33, 3.91, 1393.02, —; 16.01, 7.68, 1392.34, —; 15.42, 14.79, 1391.23, —; 14.86, 21.42, 1390.06, —; 14.34, 27.56, 1389.03, —; 13.86, 33.33, 1388.23, 0.0084; 13.40, 38.72, 1387.29, 0.0085; 12.98, 43.77, 1386.35, 0.0080; 12.53, 48.50, 1385.45, 0.0080; 12.20, 52.96, 1384.59, 0.0077; 11.85, 57.18, 1383.78, 0.0073; 11.51, 83.43, 1382.50, 0.0074; 11.18, 108.14, 1381.42, 0.0067; 10.88, 131.67, 1380.30, 0.0068; 10.59, 153.88, 1379.27, 0.0062; 10.31, 174.98, 1378.22, 0.0061; 10.05, 195.15, 1377.15, 0.0060; 9.80, 214.36, 1376.21, 0.0057; 9.56, 232.59, 1375.37, 0.0054; 9.33, 250.05, 1374.45, 0.0053; 9.11, 266.70, 1373.53, 0.0051.

Series IIa. $A \times 10^3 \text{ M}, B \times 10^3 \text{ M}, E \text{ mV}, Z$; 31.63, 0.00, 1410.27, —; 31.01, 3.91, 1409.64, —; 30.41, 7.68, 1409.07, —; 29.28, 14.79, 1407.96, —; 28.22, 21.42, 1406.89, —; 27.25, 27.56, 1405.89, —; 26.33, 33.33, 1404.91, 0.0156; 25.47, 38.72, 1403.98, 0.0147; 24.68, 43.77, 1403.03, 0.0155; 23.92, 48.50, 1402.17, 0.0148; 23.21, 52.96, 1401.37, 0.0136; 22.54, 57.18, 1400.47, 0.0143; 22.22, 70.42, 1399.85, 0.0143; 21.90, 82.43, 1399.30, 0.0135; 21.30, 108.14, 1398.20, 0.0128; 20.72, 131.67, 1397.19, 0.0118; 20.18, 153.88, 1396.14, 0.0114; 19.67, 174.98, 1395.14, 0.0111; 19.17, 195.15, 1394.07, 0.0110; 18.71, 214.36, 1393.20, 0.0104; 18.26, 232.59, 1392.29, 0.0101, 17.83, 250.07, 1391.49, 0.0096; 17.43, 266.70, 1390.40, 0.0099.

Series IIb. $A \times 10^3 \text{ M}, B \times 10^3 \text{ M}, E \text{ mV}, Z$; 31.63, 0.00, 1410.14, —; 31.01, 3.91, 1409.49, —; 30.41, 7.68, 1408.96, —; 29.28, 14.79, 1407.88, —; 28.22, 21.42, 1406.79, —; 27.25, 27.56, 1405.81, 0.0174; 26.33, 33.33, 1404.85, 0.0162; 25.47, 38.72, 1403.91, 0.0160; 24.68, 43.77, 1403.05, 0.0144; 23.92, 48.50, 1402.20, 0.0138; 23.21, 52.96, 1401.36, 0.0132; 22.54, 57.18, 1400.56, 0.0126; 22.22, 70.42, 1399.92, 0.0132; 21.90, 82.43, 1399.39, 0.0123; 21.30, 108.14, 1398.28, 0.0121; 20.72, 131.67, 1397.14, 0.0119; 20.18, 153.88, 1396.19,

* The first few data points are not taken into account in obtaining Z because a is so close to A that the value of $A - a$ cannot be obtained with reasonable accuracy.

0.0111; 19.67, 174.98, 1395.18, 0.0108; 19.17, 195.15, 1394.16, 0.0107; 18.71, 214.36, 1393.14, 0.0106; 18.26, 232.59, 1392.20, 0.0103; 17.83, 250.07, 1319.34, 0.0100; 17.43, 266.70, 1390.47, 0.0097.

Series IIIa. $A \times 10^3 M, B \times 10^3 M, E \text{ mV}, Z$; 52.37, 0.00, 1422.62, —; 51.34, 3.91, 1422.01, —; 50.35, 7.68, 1421.51, —; 48.49, 14.79, 1420.49, —; 46.74, 21.42, 1419.34, —; 45.13, 27.56, 1418.42, —; 43.61, 33.33, 1417.50, —; 42.20, 38.72, 1416.50, 0.0251; 40.87, 43.77, 1415.59, 0.0244; 39.63, 48.50, 1414.73, 0.0239; 38.46, 52.96, 1413.83, 0.0251; 37.35, 57.18, 1413.04, 0.0234, 36.82, 70.42, 1412.50, 0.0220; 36.30, 83.43, 1411.90, 0.0213; 35.31, 108.14, 1410.80, 0.0209; 34.36, 131.67, 1409.75, 0.0198; 33.47, 153.88, 1408.68, 0.0194; 32.63, 174.98, 1407.83, 0.0179; 31.82, 195.15, 1406.83, 0.0175; 31.05, 214.36, 1405.82, 0.0174; 30.32, 232.59, 1404.88, 0.0170; 29.61, 250.07, 1403.97, 0.0166; 28.95, 266.70, 1403.18, 0.0160.

Series IIIb. $A \times 10^3 M, B \times 10^3 M, E \text{ mV}, Z$; 52.37, 0.00, 1422.52, —; 51.34, 3.91, 1421.92, —; 50.35, 7.68, 1421.35, —; 48.49, 14.79, 1420.32, —; 46.74, 21.42, 1419.27, —; 45.13, 27.56, 1418.22, —; 43.61, 33.33, 1417.24, —; 42.20, 38.72, 1416.37, 0.0258; 40.87, 43.77, 1415.51, 0.0235; 39.63, 48.50, 1414.61, 0.0243; 38.46, 52.96, 1413.73, 0.0247; 37.35, 57.18, 1412.91, 0.0240; 36.82, 70.42, 1412.29, 0.0240; 36.30, 83.43, 1411.82, 0.0215; 35.31, 108.14, 1410.72, 0.0205; 34.36, 131.67, 1409.56, 0.0206; 33.47, 153.88, 1408.53, 0.0198; 32.63, 174.98, 1407.60, 0.0187; 31.82, 195.15, 1406.56, 0.0184; 31.05, 214.36, 1405.66, 0.0177; 30.32, 232.59, 1404.78, 0.0166; 29.61, 250.07, 1403.94, 0.0167; 28.95, 266.70, 1402.96, 0.0163.

Series IVa. $A \times 10^3 M, B \times 10^3 M, E \text{ mV}, Z$; 81.83, 0.00, 1433.73, —; 80.23, 3.91, 1433.13, —; 78.68, 7.68, 1432.56, —; 75.77, 14.79, 1431.53, —; 73.05, 21.42, 1430.47, —; 70.53, 27.56, 1429.48, —; 68.17, 33.33, 1428.57, 0.0432; 65.96, 38.72, 1427.68, 0.0395; 63.88, 43.77, 1426.78, 0.0391; 61.95, 48.50, 1425.94, 0.0371; 58.39, 57.18, 1424.37, 0.0325; 56.75, 83.43, 1423.20, 0.0322; 55.21, 108.14, 1422.04, 0.0326; 53.74, 131.67, 1421.02, 0.0305; 52.35, 153.88, 1419.99, 0.0298; 51.04, 174.98, 1418.95, 0.0293; 49.78, 195.15, 1417.99, 0.0284, 48.58, 214.36, 1417.06, 0.0275; 47.44, 232.59, 1416.33, 0.0255; 46.35, 250.07, 1415.34, 0.0255; 45.31, 266.70, 1414.46, 0.0251.

Series IVb. $A \times 10^3 M, B \times 10^3 M, E \text{ mV}, Z$; 81.83, 0.00, 1433.68, —; 80.23, 3.91, 1433.20, —; 78.68, 7.68, 1432.65, —; 75.77, 14.79, 1431.59, —; 73.05, 21.42, 1430.57, —; 70.53, 27.56, 1429.50, 0.0435; 68.17, 33.33, 1428.53, 0.0432; 65.96, 38.72, 1427.60, 0.0418; 63.88, 43.77, 1426.72, 0.0402; 61.95, 48.50, 1425.84, 0.0400; 58.39, 57.18, 1424.21, 0.0371; 57.56, 70.42, 1423.69, 0.0339; 56.75, 83.43, 1423.11, 0.0338; 55.21, 108.14, 1421.97, 0.0331; 53.74, 131.67, 1420.95, 0.0310; 52.35, 153.88, 1419.98, 0.0294; 51.04, 174.98, 1419.00, 0.0284; 49.78, 195.15, 1417.95, 0.0284; 48.58, 214.36, 1417.01, 0.0276; 47.44, 232.59, 1416.08, 0.0270; 46.35, 250.07, 1415.20, 0.0262; 45.31, 266.70, 1414.34, 0.0253.

and the measured emf, E . In the course of a titration, both A and B varied because of the design of the experiments (see "Experimental procedure"). Under our assumptions, these quantities are connected by the equations

$$E = E_{0a} + 59.15 \log a + a \cdot k_a + b \cdot k_b \quad (17)$$

$$A = a + abK \quad (17a)$$

$$B = b + abK \quad (17b)$$

The last two are the mass balance equations. In these equations, k_a and k_b are assumed to be constant and known, E_{0a} is a constant to be determined for each experiment, K is a constant supposedly common to all experiments, and a and b are initially unknown variables, different for each point. In a preliminary treatment, E_{0a} for each titration was determined for the first point and a was calculated from E for subsequent points. The small correction term $b \cdot k_b$ was obtained by successive approximation.

The number of OH bound per Li^+ , Z , was obtained from

$$Z = (A - a)/B \quad (18)$$

Fig. 4 gives Z as a function of $\log a$ for the various experiments. Although

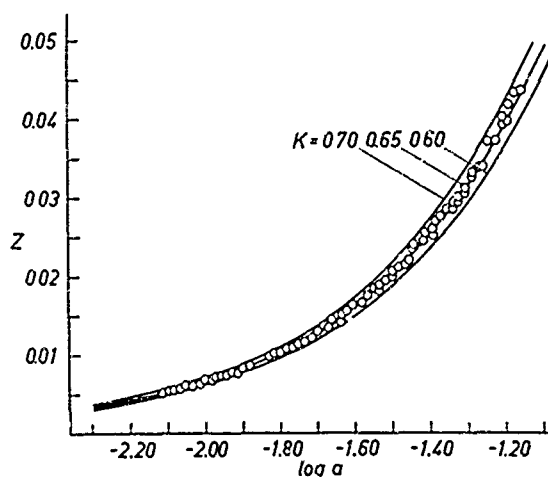


Fig. 4. Z , average number of hydroxide ions combined per total number of lithium atoms as a function of $\log a$. The solid lines have been calculated for $K = 0.60$, 0.65 , and 0.70 .

B varied considerably, the points are seen to fall on the same curve, which indicates that the assumption that only one mononuclear complex, LiOH , is formed was a reasonable one. For each separate point, K could be calculated from Z and a . Fig. 5 shows the values obtained for one series. They show

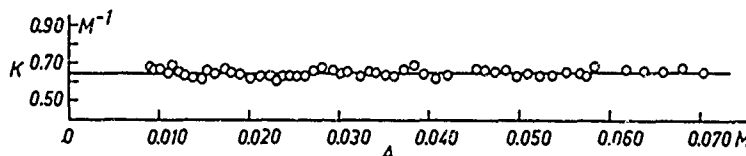
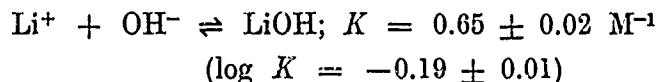


Fig. 5. Plot of K (calculated) against A in the concentration range of $0.03333 \leq B \leq 0.2667$ M. The horizontal line represents $K = 0.65$.

no systematic trend with A , and the general conclusion is



The Z ($\log a$) curves calculated assuming $K = 0.60$, 0.65 and 0.70 are shown in Fig 4. The agreement of the data with the curve for $K = 0.65$ is seen to be good.

Finally the data were treated by the generalized least squares program "LETAGROP"²⁰ The separate program was set so as to minimize the error square sum $\sum (E_{\text{exp}} - E_{\text{calc}})^2$ using eqns. (17, 17a, 17b), and not only K but

Table 2. Calculation of K and E_{0a}

System	Calculation by "hand"			LETAGROP		
	No. of points	K, M^{-1}	E_{0a}, mV	No. of points	K, M^{-1}	E_{0a}, mV
I a	11	0.65 ± 0.02	1499.32	17	$0.68_3 \pm 0.01_1$	$1499.36 \pm 0.03^{**}$
I b	16	0.66 ± 0.02	1498.82	21	$0.66_3 \pm 0.01_0$	1498.82 ± 0.06
II a	17	0.63 ± 0.02	1499.10	22	$0.65_3 \pm 0.01_1$	1499.14 ± 0.06
II b	18	0.64 ± 0.02	1499.07	22	$0.64_3 \pm 0.01_1$	1499.10 ± 0.10
III a	15	0.65 ± 0.02	1498.30	22	$0.65_3 \pm 0.01_1$	1498.83 ± 0.05
III b	16	0.66 ± 0.02	1498.69	22	$0.66_3 \pm 0.01_0$	1498.70 ± 0.03
IV a	15	0.64 ± 0.02	1498.70	20	$0.64_3 \pm 0.01_1$	1498.68 ± 0.05
IV b	17	0.66 ± 0.02	1498.66	21	$0.67_3 \pm 0.01_1$	1498.70 ± 0.03
Average value of K		0.65 ± 0.02		$0.66_4 \pm 0.01_1$		
Value accepted		0.66 ± 0.02				

* The first few data points are disregarded in the hand calculation for each K because $A - a$ is so small for these points that the value of K cannot be obtained with reasonable accuracy.

** Uncertainty of the results is given as 3σ .

also E_{0a} were used as unknown constants for each titration. Thus, in the calculation of E_{0a} not only the first point was used but also all other points of the titration. This procedure also made it possible to get an independent estimate of the standard deviations in K and E_{0a} . The results are given in Table 2, and compared with the preliminary calculation by "hand". In the preliminary calculation, the error limits given for K are estimated whereas no limits could be given for E_{0a} . In the LETAGROP treatment, the error limits given for both K and E_{0a} are 3σ .

As usual, E_{0a} varies very slowly with time but can be assumed to be constant for each titration. The E_{0a} values found from the first point and from all points of any one titration are the same, within the limits of error, except for small deviations in the first and last series. The equilibrium constant K comes out remarkably constant in the various series, and the "more objective" LETAGROP treatment has only shifted the value of K by about 0.01, thus within the limits of error.

It therefore seems that the present data can be well explained by the simple assumptions made above, thus the formation of a single complex LiOH with a formation constant

$$K = 0.66 \pm 0.02$$

and $\log K = -0.18 \pm 0.01$.

The deviations ($E_{\text{exp}} - E_{\text{calc}}$) for a typical example are shown in Table 3; the same experiment was used for Fig. 6.

It is found that the value for K is not affected much by reasonable variation of k_a and k_b . For instance, one must vary the value for k_b by about 30 %

Table 3. An example of the data (III b)

<i>A</i> M	<i>B</i> M	<i>E</i> mV	ΔE mV
0.05237	0.00000	1422.52	0.02
0.05134	0.00391	1421.92	0.01
0.05035	0.00769	1421.35	0.02
0.04849	0.01479	1420.32	-0.02
0.04674	0.02142	1419.27	-0.02
0.04513	0.02756	1418.22	0.04
0.04361	0.03333	1417.24	0.05
0.04220	0.03872	1416.37	-0.01
0.04087	0.04377	1415.51	-0.05
0.03963	0.04850	1414.61	-0.01
0.03846	0.05296	1413.73	0.03
0.03735	0.05718	1412.91	0.03
0.03682	0.07042	1412.29	0.06
0.03630	0.08343	1411.82	-0.05
0.03513	0.10814	1410.72	-0.07
0.03436	0.13167	1409.56	0.01
0.03347	0.15388	1408.53	0.00
0.03263	0.17498	1407.60	-0.06
0.03182	0.19515	1406.56	0.02
0.03103	0.21436	1405.66	-0.01
0.03032	0.23259	1404.78	-0.03
0.02961	0.25007	1403.84	0.03
0.02895	0.26670	1402.96	0.08

ΔE is defined as $\Delta E = E - E_{\text{calc}}$, where E_{calc} is a calculated value of E using E_0 which is determined by calculation using "LETAGROP". Clearly ΔE corresponds to the fluctuation of E_0 at each point.

(from -1.3 by ± 0.40) in order to make K vary by 0.02 , the error limits given.

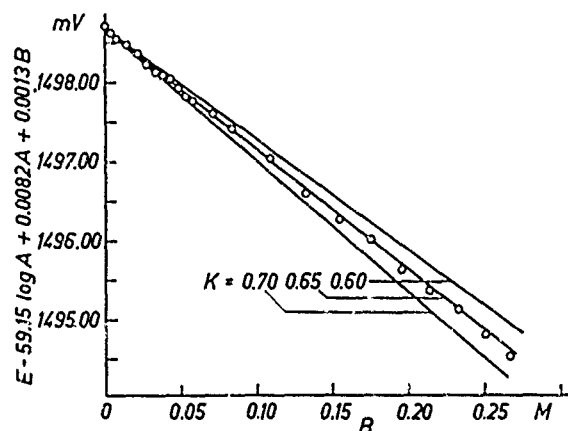


Fig. 6. Experimental results for a typical series (IIIb in Table 1). ($E - 59.15 \log A + Ak_a + Bk_b$) is plotted against the concentration of lithium ion, B . O, experimental; —, theoretically calculated ($E - 59.15 \log A + Ak_a + Bk_b$) using eqns. (17, 17a, 17b) and $K = 0.60, 0.65$, and 0.70 , respectively. In these experiments $[Ox^-]$ varied from 52.37 to 28.95 mM, and $[Li^+]$ from 0 to 266.70 mM.

Complex formation of Li^+ with Cl^- and Br^-

It may be worthwhile to go back to assumption 3) that Li^+ does not form complexes with Cl^- or Br^- .

Although the association of lithium halides has been investigated by a few workers²¹⁻²³ at the beginning of this century, these results are not very reliable, because they did not take activity factor terms into consideration.

From spectroscopic measurements, Hüttig and Keller²⁴ reported that concentrated solutions of lithium chloride have an absorption maximum at 270 nm*. For lithium bromide, the absorption maximum appeared at 280 nm for solutions of comparatively low concentration (1 to 4 M) and at 270 nm and 300 nm for higher concentration (6.27 to 11.2 M). Hantzsch²⁵, however, denied such selective absorption of lithium halide solutions.

In the present work spectrophotometric measurements were made for LiX , LiClO_4 , NaX and NaClO_4 solutions in the wavelength region between 200 nm and 350 nm, using a "Bausch and Lomb Spectronic 505". Saturated solutions of LiCl and LiBr were prepared from lithium carbonate and the corresponding acid in practically the same way as described for LiClO_4 above, and recrystallized twice from water. Saturated solutions of LiCl , LiBr and LiClO_4 showed no absorption maxima, except the characteristic absorptions of the anions (Cl^- 205 nm; Br^- 230 nm; ClO_4^- , 205 nm) which were found also with NaCl , NaBr and NaClO_4 solutions.

The absorption maxima reported by Hüttig and Keller²³ must be attributed to some other reason, for example, to free chlorine and bromine in the solutions; this source of error was pointed out by Brode²⁶ in his study of the absorption spectra of KBr and KI solutions.

From the spectrophotometric measurements no evidence could thus be found for the formation of lithium halide complexes.

Complex formation of Na^+ with OH^-

It seems possible that Na^+ might form complexes with OH^- , contrary to our assumption 2). This complex formation (which is presumably weaker than that for Li^+) would mean that what we have denoted as $\alpha = [\text{OH}^-]$ would really be $\alpha = [\text{OH}^-] + [\text{NaOH}]$. Since the total concentration of Na^+ varied only by about 10 %, the concentration of NaOH was presumably practically proportional to $[\text{OH}^-]$. The real $[\text{OH}^-]$ would then be smaller by a constant factor than the calculated α , and K correspondingly larger. This would mean only a constant factor, such as is tacitly assumed in all ionic medium work, but would not affect our conclusion on the formation of the LiOH complex.

Influence of impurities on data

The presence of impurities must also be taken into consideration. The total amounts of protolytic impurities were determined by Ciavatta's method²⁷. The results were $18 \pm 2 \mu\text{M}$ in 3 M NaClO_4 and $56 \pm 5 \mu\text{M}$ in 3 M LiClO_4 . However, it may be reasonably expected that almost all impurities are already protolyzed in the high pH region studied in this work. So, the influence on

* 1 nm = (nanometer) = 10^{-9} m = 10 Å

A and a would at most be a constant factor close to unity. An argument similar to the formation of a NaOH complex may be applied. In fact, one of the impurities in 3 M NaClO₄, $8.1 \pm 2 \mu\text{M}$, has a pK of 5.1 ± 0.2 .²⁸ From a similar argument, the impurities from the surface of an unparaffinized Jena titrating vessel were neglected, although some silicate or borate might have dissolved from the glassware.*

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* According to Ciavatta 50 μM of protolytic impurities are introduced into the solution for each titration cycle (pH 5 to 9), in an unparaffinized pyrex glass vessel, whereas in a paraffinized pyrex glass vessel only 4 μM of a protolytic impurity are added. In the present experiments, with a similar argument, even 50 μM would cause a negligible error.